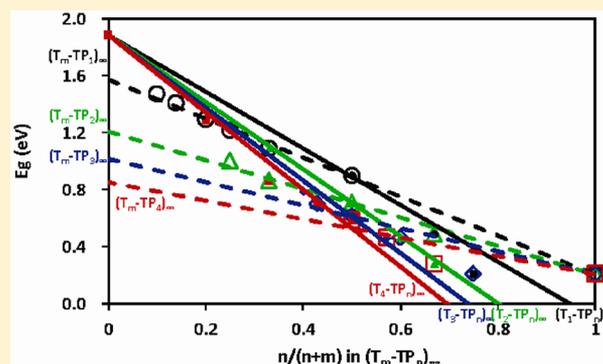


Band Gap Engineering via Controlling Donor–Acceptor Compositions in Conjugated Copolymers

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ABSTRACT: Varying composition of π -donor/acceptor moieties has been considered as an effective strategy for fine-tuning of the electronic properties of D–A conjugated copolymers. In this study, the change of optoelectronic properties with the change of donor/acceptor ratios is investigated on the basis of first-principles density functional calculations. Copolymers containing moieties of similar π -electron donating and/or accepting capabilities, e.g., thiophene (T)–methoxythiophene (OT), exhibit a linear dependence of electronic properties (especially, HOMO/LUMO, band gap, and bandwidth) on the D/A content. In contrast, for strong D/A contrast systems, e.g., thiophene (T)–thienopyrazine (TP), the electronic properties vary nonlinearly with D/A compositions. However, when the block size of one parent monomer in a strong D/A contrast system is fixed, the variation of electronic properties shows a remarkable linear correlation against D/A compositions. We found that the deviation of electronic properties from a linear composition dependence is dominated by the strength of orbital interactions between D and A. Weak orbital interactions between D and A moieties tend to lead to a nonlinear composition dependence. Our results provide useful insights for band gap tuning through the adjustment of D/A compositions in D–A conjugated copolymers.



1. INTRODUCTION

Photovoltaic devices consisting of low band gap conjugated polymers blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) or [6,6]-phenyl C₇₀-butyric acid methyl ester (PC₇₀BM) have been demonstrated with a power conversion efficiency of around 3–7%.¹ However, the efficiency of polymer solar cells is still a step away from the commercialization target of 10%. On the basis of correlations between the open-circuit voltage (V_{oc}) of different bulk-heterojunction solar cells with the oxidation potential/HOMO position of the donor polymer, Scharber et al.² demonstrated that the theoretical efficiency of bulk-heterojunction devices using PCBM as an electron acceptor is dominated by the HOMO/LUMO levels of the conjugated polymer. The photoactive material should have a lowest unoccupied molecular orbital (LUMO) lower than –3.9 eV and a band gap (E_g) around 1.5 eV (1.2–1.8 eV). Proper molecular orbital alignment between the polymer (electron donor) and PCBM (electron acceptor) could provide the optimal solar cell efficiency.

The conjugated polymers consisting of alternating donor (D) and acceptor (A) moieties show great potential for use in photovoltaics.³ The π -electron donating/withdrawing substituents on the backbone induce charge transfer between D–A moieties, leading to a mesomerism⁴ in the ground state. The delocalization of π -electrons in such polymers results in reduced bond length alternation and band gap.^{3c,5} Such copolymers are especially attractive because their band gaps,

one of the dominating factors for the efficiency of the solar cells, are tunable by changing the chemical composition and molecular structure of the D or A moieties. For example, fluorene–thiophene based copolymers showed a wide range of E_g from 2.7 to 0.76 eV by changing the substituents on thiophene.^{4,6} Nonetheless, engineering the HOMO/LUMO energy levels and band gap of D–A conjugating copolymers toward desired values has been quite challenging because there does not seem to be a simple quantitative relation between these properties, the chemical composition, and molecular structure.

Attaching electron rich groups (such as alkoxy phenyl or thiophenyl groups) on the acceptor of D–A conjugated polymer provides another strategy for band gap tuning.⁷ The π -electron may transfer from electron rich groups to the electron deficient acceptor, promoting the π -electron delocalization over the backbone. As a consequence, a red-shift and wider absorbance range in the UV–vis spectrum can be obtained. It is also noted that the pendant substituted π -rich donating groups can potentially hinder the stacking of intermolecular and reduced carrier mobility.^{7a}

Introducing pendent groups to the polymer chain is yet an alternative means for tuning the energy levels of the copolymer.

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Zhou et al.⁸ found that the introduction of alkyl side chains on different positions of the polymer would change the coplanarity of the backbone, and electronic and optical properties of conjugated polymer could also be changed significantly at the same time. Zhu et al.⁹ found that copolymers containing benzene and fluorene would result in lower HOMO and higher LUMO because of the disturbance of the coplanarity along the polymeric backbone.

More recently, a new strategy for modifying energy levels of conjugated copolymers is proposed by changing the composition of D/A units in the backbone. It is shown that both the absorption and luminescence spectra and electronic properties can be systematically tuned by varying the composition ratio of D/A units.¹⁰ For example, a series of thiophene (T) and thienopyrazine (TP) based donor–acceptor conjugated copolymers was synthesized at different TP/T ratios.¹¹ Such a D–A copolymer has a lowest band gap of 1.1 eV when the TP/T ratio is 1/1. The band gap increases to 1.8 eV as the TP/T ratio becomes 1/4. These studies indicate that the optical band gap and electronic properties of these copolymers exhibit a predictable dependency on its chemical compositions.

Several theoretical studies have been performed to understand the underlying physics governing the composition effects in D/A copolymers. Meyers et al.¹² employed semiempirical quantum computations to the stereoregular copolymers of poly(*p*-phenylene vinylene) (PPV) and poly(2,5-dimethoxy-1,4-phenylene vinylene) (DMPPV) and found that the electronic properties (band gap and front orbital energies) are simply the linear interpolation between those of the homopolymers. dos Santos et al.¹³ showed that, for the same PPV and DMPPV copolymers, random and cluster arrangements, which lead to orbital localization, may result in a nonlinear compositional dependence. Gil-Bernal et al.¹⁴ designed several stereoregular copolymers with varying degree of structural similarities of parent monomers and found that band gaps of copolymers with similar chemical structures reveal a closely ideal linear relationship against the composition of parent monomers, whereas structurally dissimilar parent monomers lead to deviation from the linear dependency. These studies seem to suggest that stereoregular copolymers with structurally similar D/A moieties exhibit a linear composition dependence in the electronic properties. The structure dissimilarities and/or irregular (random or cluster) arrangements of D/A units would lead to a nonlinear composition dependence. Karsten et al. investigated the composition effect on the band gap of T–TP copolymers.¹⁵ They found that the deviation of the band gap from linear dependence on composition in T–TP systems is a result of the absence of clear donor–acceptor characters in thiophene and thienopyrazine units.

In this study, we investigate the fundamental reasons for the different composition dependences in the optical and electronic properties of D–A conjugated copolymers. We discover that these seemingly different behaviors can all be understood by the strength of orbital interactions between the D/A moieties. For moieties having similar HOMO/LUMO energy levels (which are often structurally similar), their conjugated copolymers show stronger orbital interactions over a large range of D–A compositions and energy levels display a closely linear correlation at different D–A ratios. For moieties having very different HOMO/LUMO energy levels (e.g., structurally dissimilar, strong D/A contrast, etc.), the conjugated

copolymers contain weaker orbital interactions at low and high D/A ratio region, leading to their nonlinear composition dependence. In other words, the fundamental reason for the nonlinear behaviors should be the orbital energy differences (in frontier orbitals) of monomers, and the chemical structure or cluster arrangements are the possible causes for the energy differences. Furthermore, even for the weak orbital interacting systems, we discovered linear correlations in band gap against compositions when the block size of one of the parent monomer was kept constant. Therefore, the band gap of such copolymers can be predictable and controllable by varying the D/A composition in the copolymer. The results presented here can serve as useful information for estimation of the optoelectronic properties of donor–acceptor alternating copolymers under different D–A compositions.

2. COMPUTATIONAL DETAILS

In this work, we investigate the composition effect on the electronic properties for two D–A conjugated copolymers: thiophene (T)/thienopyrazine (TP) (strong D/A contrast) and thiophene (T)/methoxythiophene (OT) (weak D/A contrast). All electronic and optical properties of conjugated polymers are carried out by the quantum mechanics program Gaussian 09.¹⁶ The geometry optimization for each polymer at the ground state was performed using density functional theory (DFT) at the B3LYP/6-31G* level. It has been shown that B3LYP/6-31G* gave proper structural properties of conjugated polymers.¹⁷ Electronic properties including HOMO/LUMO levels, bandwidth, and band gap are obtained by single point calculation at the B3LYP/6-311+G* level. The electronic properties of thiophene (T) based oligomers are calculated for (T–X)_n with *n* = 1–4 and X = TP (thienopyrazine) or OT (methoxythiophene). The properties of a corresponding polymer of an infinite chain length are obtained by linear extrapolations (property vs inverse of the number of rings). The linear extrapolation method has been successfully employed in investigating several series of polymers.¹⁸

3. RESULTS AND DISCUSSION

The structures of two thiophene-based copolymers studied in this work are summarized in Figure 1. In the following

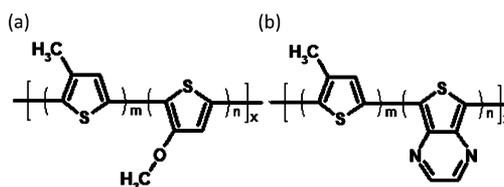


Figure 1. Sketch of chemical structures of thiophene-based copolymers studied in this work. (a) Methylthiophene (T)–methoxythiophene (OT) and (b) methylthiophene (T)–thienopyrazine (TP).

discussions, the copolymers are denoted as (T_m–OT_n)_x and (T_m–TP_n)_x, where T, OT, and TP represent methylthiophene, methoxythiophene, and thienopyrazine, respectively. The subscripts *m*, *n*, and *x* are the number of units. For example, (T₁–OT₁)_∞ refers to a stereoregular copolymer of alternating T and OT with a degree of polarization of infinity and a T/OT ratio of 1/1. The composition effect is investigated by varying the ratio of *m*/*n*. The properties of polymers calculated in this work are summarized in Table 1. Note that, to test the effect of

Table 1. Electronic Properties of Copolymers in Different D–A Fractions Considered in This Study

copolymer composition $m, n [n/(n+m)]$	$(T_m-OT_n)_1/(T_m-TP_n)_1^a$		$(T_m-OT_n)_\infty/(T_m-TP_n)_\infty^a$			$E_g(H-L)$	BW of VB	BW of CB
	$-E_{HOMO}$	$-E_{LUMO}$	$-E_{HOMO}$	$-E_{LUMO}$				
$m = 1, n = 0 [0.0]$	6.47	0.52	4.51 (5.03) ²⁶	2.62 (2.55) ²⁶	1.88 (2.48) ²⁶	2.10	1.76	
$m = 4, n = 1 [0.2]$	4.79/4.87	2.04/2.86	4.37/4.39	2.64/3.10	1.73/1.29	1.63/1.83	1.72/0.73	
$m = 3, n = 1 [0.25]$	5.11/4.91	2.01/2.81	4.28/4.37 (4.76) ^{19a}	2.66/3.16 (3.02) ^{19a}	1.62/1.21 (1.74) ^{19a}	2.13/1.85	1.85/0.89	
$m = 2, n = 1 [0.33]$	5.49/5.12	1.68/2.78	4.20/4.33	2.68/3.24	1.51/1.09	2.20/2.07	1.94/0.95	
$m = 1, n = 1 [0.5]$	5.58/5.63	1.44/2.78	4.15 (4.82) ²⁷ /4.30 (4.64) ^{19a}	2.63 (3.12) ²⁷ /3.41 (3.11) ^{19a}	1.53 (1.70) ²⁷ /0.89 (1.53) ^{19a}	2.04/2.37	1.91/0.96	
$m = 2, n = 3 [0.6]$	4.66/4.84	2.26/3.37	4.06/4.17	2.67/3.71	1.39/0.46	1.90/2.41	2.07/1.38	
$m = 1, n = 3 [0.75]$	4.72/4.95	2.09/3.36	3.95/4.09	2.67/3.88	1.28/0.21	2.15/2.55	2.13/1.70	
$m = 0, n = 1 [1.0]$	6.11/3.95	0.49/4.16	3.86 (4.56) ²⁷ /4.16	2.58 (2.98) ²⁷ /3.95	1.28 (1.58) ²⁷ /0.21 (0.69) ²⁸	2.53/2.15	1.45/2.07	

^aNumbers in parentheses are experimental data in the literature. All values are in units of eV.

block sizes of parent monomers, we consider different block sizes of donor and acceptor for the same D/A ratio of several D/A combinations. For example, we calculate band gaps for D/A = 1:1 with four block sizes: $(T_1-X_1)_\infty$, $(T_2-X_2)_\infty$, $(T_3-X_3)_\infty$, and $(T_4-X_4)_\infty$.

3.1. Composition Effect to the HOMO–LUMO Band Gap. The composition effect to THE HOMO–LUMO band gap in $(T_m-OT_n)_\infty$ and $(T_m-TP_n)_\infty$ is shown in Figure 2. Generally, calculated band gaps are in good agreement with the

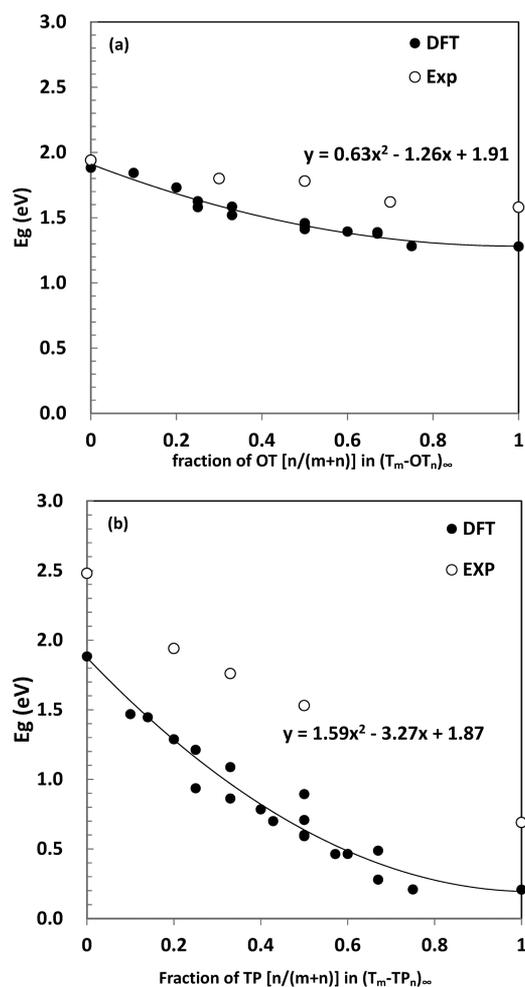


Figure 2. The evolution of DFT calculated HOMO–LUMO band gap for copolymers (a) $(T_m-OT_n)_\infty$ and (b) $(T_m-TP_n)_\infty$ as a function of OT or TP fractions.

available experimental results,¹⁹ albeit a consistently lowered calculated value (by 0.3–0.4 eV for $(T_m-OT_n)_\infty$ and by 0.5–0.6 eV for $(T_m-TP_n)_\infty$) compared to the experiments. Note that the calculations were done in the gas phase, while experiments were performed in dilute solutions. The good agreement between our calculation and experiment could be a result of error cancellation or an indication that the solvent has little impact on the electronic properties of the systems studied here. We employ second order polynomial fitting on calculated band gaps (solid curves). The clear differences in curvatures for $(T_m-OT_n)_\infty$ and $(T_m-TP_n)_\infty$ indicate a relatively linear composition dependency in the T–OT system and a nonlinear dependency in T–TP. In addition, there is a significant drop in band gap with about 0.4 eV observed at low TP fractions (<0.2). As the fraction of TP is higher than 0.75, the band gaps remain almost constant.

Previous studies have showed that electronic structures of copolymers are determined by the fraction and arrangement of the parent moieties.²⁰ Linear interpolation between the band gaps of the parent polymers is observed in stereoregular copolymers with similar chemical structures.^{12,14} For random copolymers, formation of moiety clusters would cause spatial electronic localization of the molecular orbitals which would lead to electronic structures deviating away from linear composition dependency.²⁰

Interestingly, if we select copolymers having the same length of one moiety (T or TP), band gaps of all these selected copolymers show linear composition dependency. Figure 3 shows the linear correlations for copolymers $((T_1-TP_n)_\infty, (T_2-TP_n)_\infty, (T_3-TP_n)_\infty, (T_4-TP_n)_\infty)$ and for copolymers $((T_m-TP_1)_\infty, (T_m-TP_2)_\infty, (T_m-TP_3)_\infty, (T_m-TP_4)_\infty)$. In most cases, the correlation coefficients are nearly unity. For four straight lines starting from TP = 0, a larger block size of T leads to a correlation line with a larger slope. On the other hand, the otherfour straight lines starting from TP = 1 show the opposite trend: the larger block size of TP results in a line with a smaller slope. The reason for the different composition dependences in these copolymers can be better understood from the orbital interactions discussed in later sections.

3.2. Orbital Interactions and π -Electron Delocalization. Figure 4 illustrates the energy levels of monomer, dimer of T, OT, TP, and their comonomer $(T_1-OT_1)_1$ and $(T_1-TP_1)_1$. The HOMO of OT_1 is -6.11 eV which is higher than the HOMO of T_1 , -6.47 , by 0.36 eV. The LUMO levels of them are similar, with a difference of 0.03 eV. In contrast, the pyrazine substituent on T has a similar HOMO level to that of T (differ by 0.08 eV) but a significantly lower LUMO level

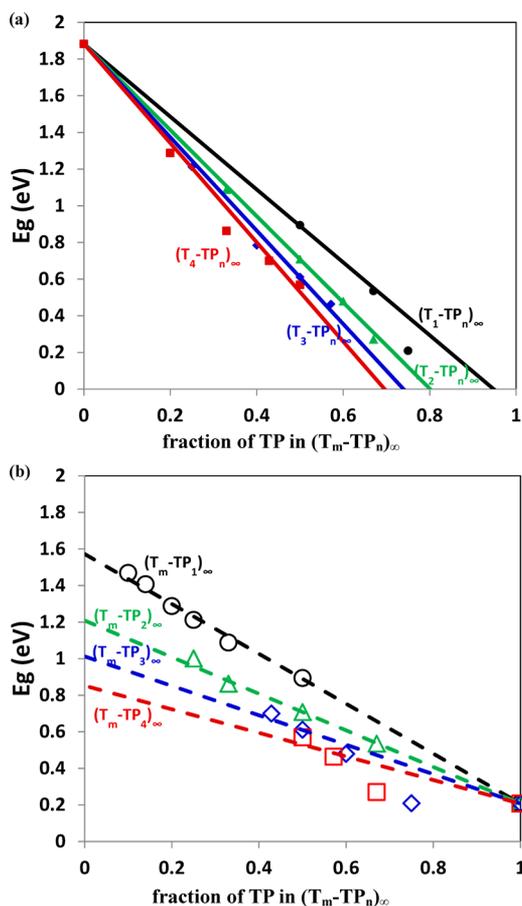


Figure 3. Variation of the band gap of $(T_m-TP_n)_\infty$ copolymers with the fraction of TP. The data are the same as those in Figure 2b but are reorganized in a way that the block size of segment T (T_1-TP_n , T_2-TP_n , T_3-TP_n , T_4-TP_n) (a) or TP (T_m-TP_1 , T_m-TP_2 , T_m-TP_3 , T_m-TP_4) (b) is kept at a constant value. The lines are a linear fit to the band gaps for copolymers having the same block size of one of the constituting monomer.

(lower by 2.12 eV). Therefore, thiophene is a donor in T-TP but an acceptor in T-OT copolymers. The HOMO-LUMO (H-L) gaps are 4.14 eV for $(T_1-OT_1)_1$ and 2.85 eV for $(T_1-TP_1)_1$. The much smaller H-L gap of the latter is a result of the strong π -electron accepting nature of TP_1 , implying a large degree of charge transfer in $(T_1-TP_1)_1$. The calculated excess of π -electrons ($\Delta\pi$)⁴ on the thiophene (obtained by Mulliken population analysis²¹) of $(T_1-TP_1)_1$ (+0.05) is found to be larger than that of $(T_1-OT_1)_1$ (-0.02). The difference in the energy levels of the monomer moieties also implies the degree of molecular orbital interactions during the formation of the dimer. Similar energy levels in the monomers would have a better molecular orbital interaction, resulting in a delocalized π -electron distribution in the dimer. For example, T and OT have similar HOMO and LUMO levels (Figure 4a) and the HOMO and LUMO of T_1-OT_1 spreads on both T and OT. In contrast, TP_1 and T_1 have similar energy levels in their HOMO but very different LUMOs (by 2.26 eV) (Figure 4b). Therefore, the LUMO is localized on TP but the HOMO is delocalized.

It is noteworthy that both of the H-L gaps of dimers $(T_1-TP_1)_1$ and $(T_1-OT_1)_1$ are smaller than those of the original moieties T_1 , OT_1 , and TP_1 but between that of dimer pairs T_2 , OT_2 , and TP_2 , respectively. Extending the results from oligomers to polymers, all the band gaps and the positions of

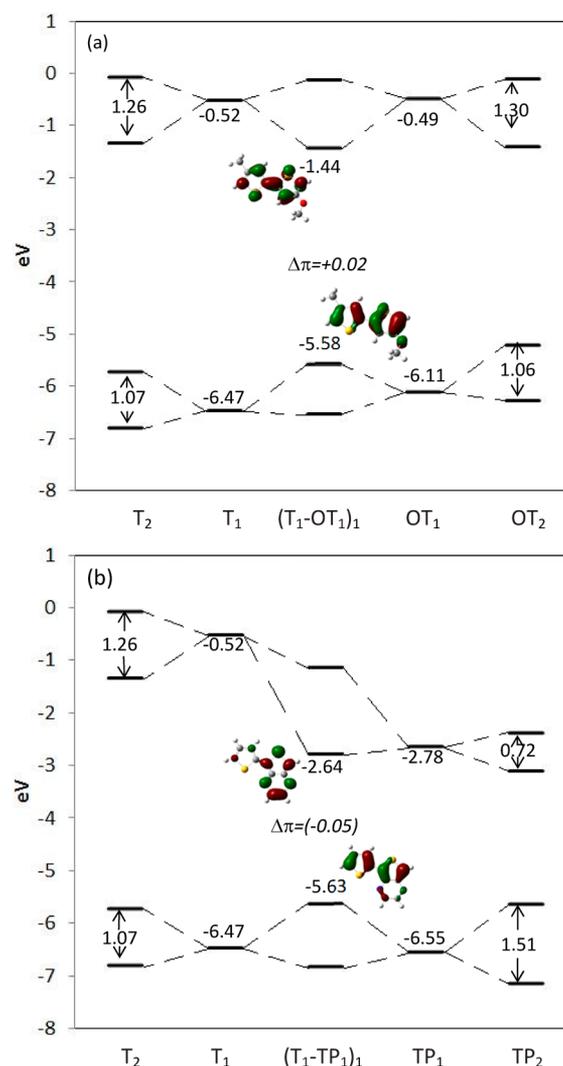


Figure 4. Energy level of frontier orbitals of different monomers from DFT calculations: (a) thiophene (T), methoxythiophene (OT), and their comonomer $(T_m-OT_n)_1$; (b) thiophene (T), thienopyrazine (TP), and their comonomer $(T_m-TP_n)_1$. Electron distributions of HOMO/LUMO orbitals of $(T_1-OT_1)_1$ and $(T_1-TP_1)_1$ generated at isovalue = 0.04 are shown next to the corresponding energy levels.

HOMO/LUMO of different D/A composition are also between the pure homopolymers T_∞ , OT_∞ , and TP_∞ (Figure 2). In other words, a smaller band gap (compared to the corresponding homopolymers) in alternative donor-acceptor conjugated chains is not observed in these two systems, which is similar to the finding of Salzner.²²

3.3. Variation of Strength of Orbital Interactions with Composition. We illustrate the change in the strength of orbital interactions with compositions using three systems: T_3-X_1 (75% of T), $(T_1-X_1)_2$ (50% of T), and T_1-X_3 (25% of T). In addition, the block size effects are analyzed by comparing two systems: $(T_1-X_1)_2$ (block size of 1) and T_2-X_2 (block size of 2). Among the several factors influencing the strength of orbital interaction (such as the symmetry of the orbitals, the energy difference between them, their orbital sizes, and the distance between the orbitals), the relative energy of pi orbitals on the D and A moieties dictates the strength of interaction.²³ On the basis of our previous studies for thiophene derivatives,^{4,24} if the energy difference between the HOMO

(or LUMO) of the two monomers is less than about 1 eV, strong orbital interaction and better electron delocalization can be expected in the HOMO (or LUMO) of the dimer.

Figure 5 shows the comparison of energy levels of these four systems for T–OT and T–TP systems. From Figure 5a, the

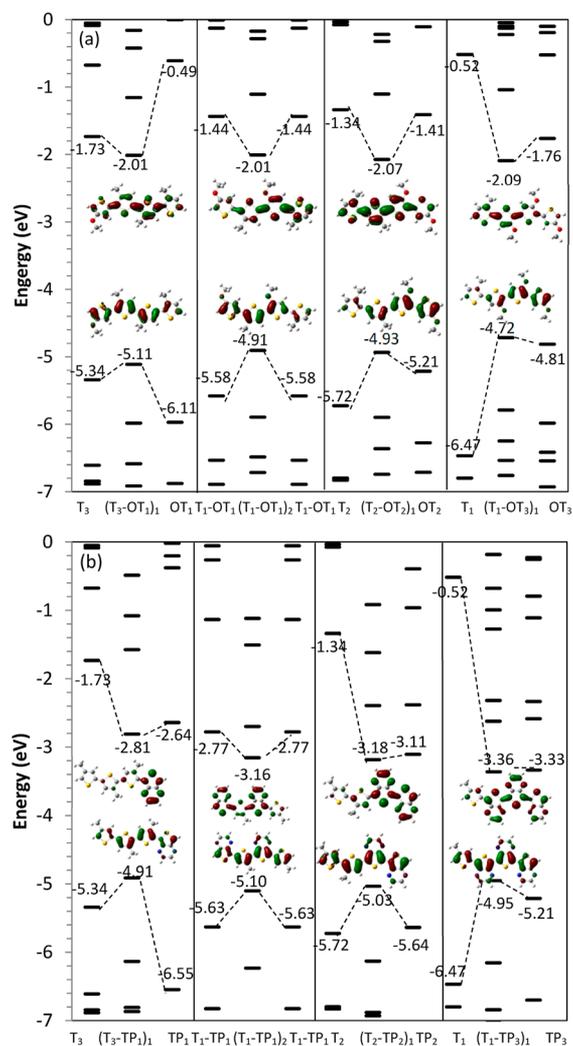


Figure 5. Comparison of energy levels of different combinations of tetramers ($m + n = 4$) in $(T_m-OT_n)_1$ systems (a) and $(T_m-TP_n)_1$ systems (b).

variation in HOMO, LUMO, and H–L gap of T–OT tetramers (with varying composition and block size) is relatively small, within 0.47 eV. As can be seen, the HOMO and LUMO of all tetramers are delocalized throughout the tetramer in all cases, indicating the better molecular orbital interactions between T and OT moieties. Contrary to T–OT systems, T–TP displays distinct behaviors of orbital interactions as the composition of T/TP changes (Figure 5b). While the HOMOs of tetramers are delocalized in all cases, the LUMOs are mostly localized (with varying degrees) around the units of TP, with $(T_1-TP_1)_2$ showing the best LUMO delocalization. The identical LUMO energy of $(T_1-TP_1)_1$ units implies better orbital interactions, and therefore better orbital delocalization. In other cases ($(T_3-TP_1)_1$, $(T_2-TP_2)_1$, and $(T_1-TP_3)_1$), there is a larger discrepancy between HOMOs and LUMOs of donor and acceptor moieties, resulting in weak orbital interactions. The $(T_1-TP_3)_1$ case is

an outstanding example. The LUMO of TP_3 is lower than that of T_1 by 2.81 eV. As a consequence, the LUMO of $(T_1-TP_3)_1$ is nearly the same as that of TP_3 . The change in the strength of orbital interactions with the fraction of TP in the T–TP systems thus implies a more complicated composition dependence.

Tetramers of $(T_1-OT_1)_2$ and $(T_1-TP_1)_2$ are formed by a dimer of T_1-OT_1 and T_1-TP_1 . The complete match of HOMOs and LUMOs of the dimers therefore leads to good hybridization of frontier orbitals and the resulting electron density uniformly spread all over the backbone (see Figure 5). However, as the parent unit changes from monomer to comonomer (increasing block size), a larger mismatch between LUMOs of T_2 and TP_2 would be observed. The localized electron density on the TP_2 units for the LUMO of $(T_2-TP_2)_1$ indicates that the LUMO is almost contributed by that of TP_2 . One can expect that the LUMO of $(T_m-TP_m)_\infty$ would be similar to that of TP_m . Therefore, we could expect that the LUMO and H–L gap have a dependency on the block sizes. Such variation in the electronic properties with block size is not prominent in T–OT systems, as the orbital energies are similar.

Therefore, we find that the strength of orbital interactions between donor–acceptor is the dominating factor to the electronic properties of D–A copolymers with varying D/A compositions. Strong orbital interactions between frontier orbitals of repeating units reveal well mixed molecular orbital character, and exhibit a linear dependence against compositions. For the systems with a larger difference in energy levels (e.g., T–TP), both composition and block size would easily lead to the mismatch of orbital energy and reduce orbital interaction. The weak orbital interactions would disturb the linear dependence against composition.

3.4. Bandwidth and Frontier Orbitals. Bandwidth is another measurement of strength of orbital interactions between repeating units. Wide bandwidth normally results from hybridization of orbitals of similar energies (strong orbital interactions). A polymer of wide bandwidth also possesses higher intramolecular charge mobility. For example, too strong contrast between donor and acceptor (weak orbital interaction) in D–A conjugated copolymer has been found to result in narrowed bandwidth and lowered carrier mobility in valence and conduction band.²⁵ Figure 6 illustrates the extrapolated bandwidths as a function of the composition of the stereoregular chains. To remove the bias resulting from the difference in the size of the copolymers, bandwidths for fractions of 0.2, 0.33, 0.5, 0.66, and 0.75 for $(T_m-OT_n)_\infty$ and $(T_m-TP_n)_\infty$ are multiplied by 5/2, 3/2, 1, 3/2, and 4/2, respectively.²⁵ Wider bandwidths are observed for homopolymers of $(T)_\infty$, $(TP)_\infty$, and $(OT)_\infty$ because of the better orbital interactions. Except for the conduction bands of $(T_m-TP_n)_\infty$, which are lower than 1.5 eV, all the bandwidths are around 2.0 eV. The narrowed bandwidths of the conduction band of (T_m-TP_n) copolymers are attributed to the weak interactions between LUMOs of TP and T (see the lower LUMO of TPs in Figure 5b). As can be seen, the bandwidth can be as low as 0.22 eV in the case of $(T_3-TP_1)_\infty$. In such a case, the LUMO is localized at TP (Figure 7) and the separation of localized LUMO results in the weak orbital interactions as the chain length increases. As a result, the bandwidth of T–TP copolymers with a small fraction becomes very small and may become a trap state for electron transport.

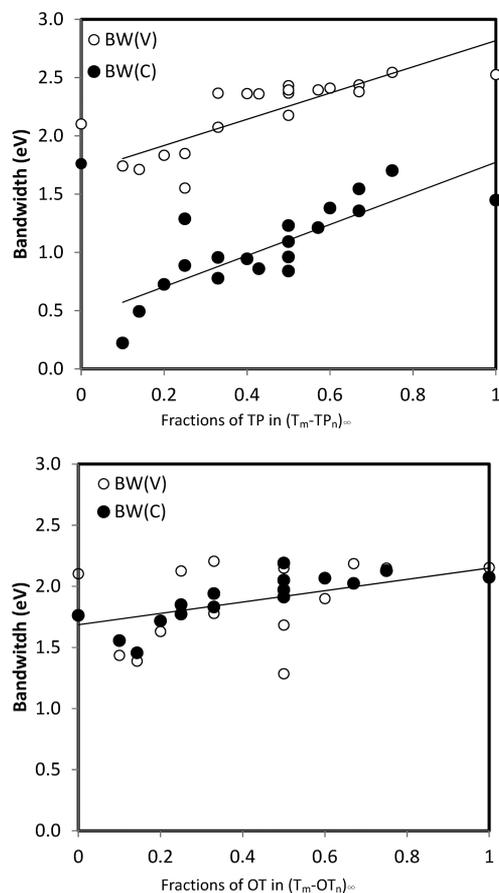


Figure 6. Calculated valence (V) and conduction (C) bandwidth (BW) as functions of the fraction of TP in $(T_m-TP_n)_\infty$ (a) and OT in $(T_m-OT_n)_\infty$ (b).

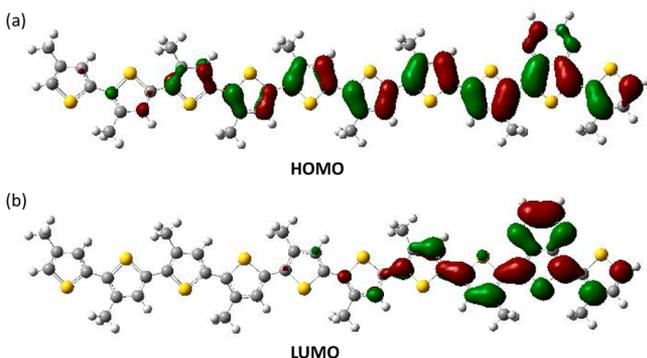


Figure 7. Electron distribution of HOMO (a) and LUMO (b) orbitals of selected oligomers $(T_9-TP_1)_1$ at isovalue = 0.02.

4. CONCLUSION

The composition effect on two stereoregular alternating copolymers of thiophene–thienopyrazine (T–TP) and thiophene–methoxythiophene (T–OT) is studied by density functional theory. Our theoretical study shows that energy level fine-tuning of D–A conjugated copolymers can be achieved by adjusting the composition between donor and acceptor. For these two copolymers, T–TP and T–OT could be referred to as strong and moderate D–A contrast systems, respectively. The hybridization between HOMO/LUMO states of the parent monomers plays a critical role in the variation of optoelectronic properties with the D/A composition. The

composition effect on D–A conjugated copolymers can be summarized as follows:

- (1) For a moderate D–A contrast system (e.g., T–OT), the band gap of the copolymer exhibits nearly linear behavior against D/A composition. The strong orbital interactions between the D and A moieties (as a result of the similar energies of the orbitals) lead to a resulting frontier orbital energy that falls between those of D and A (see Figure 4a). The well-mixed orbital interactions thus result in linear composition dependence with the D/A compositions.
- (2) For a strong D–A contrast system (e.g., T–TP), the band gap of the copolymer decreases rapidly as the fraction of TP increases, deviating from the linear composition dependence as seen in the T–OT system. The weak orbital interactions between the D and A moieties (as a result of the different energies of the orbitals) lead to a resulting HOMO that is close to the higher HOMO of D or A and a LUMO that is close to A (see Figure 4b). The poor orbital interactions thus result in the deviation from linear composition dependence with the D/A compositions.
- (3) A narrow bandwidth of conduction band is observed at low acceptor (TP) fraction region for T–TP systems. In this case, the LUMO is localized on TP (whose fraction in the main chain is small) and thus the narrow bandwidth is a result of the weak interactions between the localized molecular orbitals on TP.

Our study indicates whether electronic properties follow linear dependence by varying D/A compositions dominated by the strength of orbital interactions between D and A. Even though nonlinear behavior against D/A compositions would be observed under different block sizes of parent monomer in a strong D/A contrast system, keeping block sizes of parent monomer and then changing compositions of the other copartner in stereoregular copolymers would be considered as a better strategy to adjust the band gap in a linear manner. Low carrier mobility might also emerge from electron localized states in low acceptor composition. As a result, our theoretical study indicates that orbital interactions corresponding to relative energy levels of donor and acceptor play the most important role on the electronic properties through varying donor/acceptor ratio in D–A conjugated copolymers.

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Notes

The authors declare no competing financial interest.

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